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FERROZIRCONIUM CERAMIC PIGMENTS

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A new technology for producing ceramic pigments in the $ZrO_2 – SiO_2 – Fe_2O_3$ system is described, which is successfully implemented in production.

Specific properties of ceramic pigments depend on the type of their crystalline lattices. S. G. Tumanov [1] proposed to classify pigments not on the basis of their colorant elements or tints but on the basis of their structural features: spinel, granite, corundum, willemite, sphene, mullite, and zirconium pigments. Pigments based on the zircon crystalline lattice are of special interest, as they are especially resistant to the effect of high temperatures, melted glazes, and fluxes.

Studies of zirconium pigments demonstrated that colorant ions (chromophores) can be “locked” inside the zircon lattice in the course of synthesis of zircon from zirconium dioxide and silicon dioxide [2]. This motivated the development of heat-resistant pigments of this type. Owing to a number of properties (resistance to high temperatures, resistance to a gas medium, etc.) they soon found extensive application in the decoration of ceramics.

The pigments based on zirconium dioxide can be divided into two groups. The first group represents pigments containing silica. In firing, zircon is formed in them. This group includes zirconium-vanadium sky-blue and green, zirconium-praseodymium yellow, ferrozirconium pink, and selenium-cadmium-zirconium red pigments. The compositions of the second group do not contain silica: they are zirconium-vanadium yellow pigments.

There exist different points of view concerning the formation mechanism and the origin of tinting of zirconium pigments. Numerous researchers studied the synthesis and specifics of these pigments.

With respect to the origin of the sky-blue color of the $ZrO_2 – SiO_2 – V_2O_5 – NaF$ system, most researchers share the same opinion. Its essence is that vanadium in this system exists in a solid solution and the sky-blue color is caused by the ions of tetravalent vanadium, which in the course of synthesis in the reduction of V_2O_3 is incorporated in the zircon structure.

Opinions concerning the origin of the green tint of oxides in the $ZrO_2 – SiO_2 – V_2O_5$ system differ. Some scientists believe that the green pigment contains a mixture of zircon and monoclinal zirconium dioxide and represents a combination of sky-blue and yellow pigments. Other researchers think that the green color is determined by the simultaneous presence of the sky-blue crystals of zircon, which is a carrier of a sky-blue color, and an excessive content of V_2O_5 that is a carrier of yellow color. An assumption has been made that two types of zircon having different forms and tints are synthesized in the $ZrO_2 – SiO_2 – V_2O_5 – NaF$ and $ZrO_2 – SiO_2 – V_2O_5$ systems.

There are known experiments in obtaining yellow pigments in the $ZrO_2 – V_2O_5$ system. Some authors report that the crystalline phase in the yellow pigment does not change after firing and consists of monoclinal zirconium dioxide. A contradictory opinion asserts that the main role in the formation of the pigment is played by a transformation of zirconium dioxide from a monoclinal modification to a tetragonal one and vice versa, and the formation of the pigment is related to the destruction and growth of newly forming crystals.

A relatively new type in the group of pigments with the zircon crystalline lattice is represented by ferrozirconium (FZ) pink-colored pigments. The majority of researchers believe that Fe_2O_3 becomes incorporated in the crystal lattice of zirconium silicate during the synthesis of the pigment. Thus, it is assumed that FZ pigments are identical in their nature to other zirconium pigments. However, the fact that their production requires a more complicated technology using special techniques not previously known in the ceramic pigment production disproves this assumption.

An analysis of the literature and patent data established that the least investigated and the most controversial issues in production of FZ pigments are the mechanism of their formation and the nature of their coloring.

It is established [3] that the tint of a FZ pigment is allochromatic. The pink color is mainly caused by iron dioxide in its α-form (hematite) forming inclusions in a zircon crystal. Furthermore, the color is influenced by associates of

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TABLE 1

Pigment	Color	Temperature interval of application, °C
VK-2	Light sky-blue	700 – 1250
VK-13	Crimson	700 – 1050
VK-16	Pink	700 – 1250
VK-24	Lemon yellow	700 – 1250
VK-23	Yellow	700 – 1250
VK-28	Orange-yellow	700 – 1250
VK-29	Sun-yellow	700 – 1050
VK-30	Yellow-orange	700 – 950
VK-32	Ink	700 – 1250
VK-33	Lilac	700 – 1100
VK-41	Blue	700 – 1100
VK-42	Light blue	700 – 1100
VK-44	Blue-sky-blue	700 – 1250
VK-51	Bluish-green	700 – 1250
VK-52	Marine (sea wave)	700 – 1250
VK-53	Turquoise	700 – 1250
VK-59	Chrome-green	700 – 1100
VK-60	Green	700 – 1100
VK-73	Brown-black	700 – 1150
VK-74	Black	700 – 1150
VK-95	Red-brown	700 – 1150
VK-98	Beige-straw-colored	700 – 1300
VK-99	Straw-colored	700 – 1300

trivalent iron presumably located in the dislocations of the zircon crystal lattice and concretions of zircon crystals that encompass an additional quantity of hematite grains. The latter contribute to intensifying the pigment color.

Of the three main components (ZrO_2, SiO_2, and Fe_2O_3), only silicon is mobile at high temperatures. Therefore, it was concluded that the determinant factor is the direct contact between the grains of hematite and zirconium dioxide. Only when this condition is satisfied does the formation of zircon crystal with hematite inclusions become possible due to the interaction between the immobile zirconium and the introduced silicon. The mechanism of the formation of a FZ pigment consists in the synthesis of zircon crystals of a strict geometrical shape from zirconium dioxide, whose grains are previously bonded (joined) with Fe_2O_3 and SiO_2 particles. The hematite particles in this case are trapped by the zircon crystals.

The only factor needed for the formation of a pigment is the dry preparation of the batch, implying attrition of the particles instead of crushing of the components. In other word, the batch requires a special preparation, in which its component are not simply mixed (or milled) but become rubbed into each other, i.e., enter in a physical content. The quality of the batch processing remains the most important criterion for a successful synthesis of the pigment.

The obtained results became a basis for the development of a new technology of pigment synthesis and setting up the industrial production of the FZ pigment. The new technology includes the following operations: selection of a method and parameters for the batch preparation, determination of the optimum parameters of the batch components (materials),

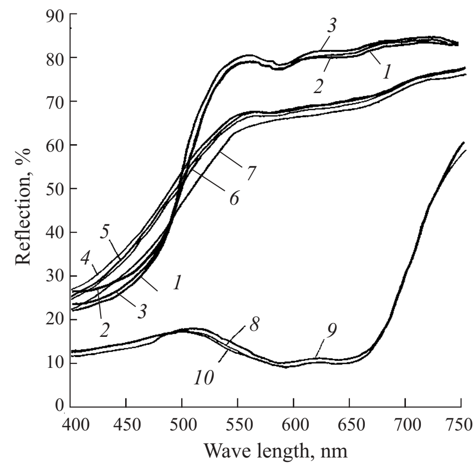

Fig. 1. Spectra of diffuse reflections of pigments: *1*, *2*) experimental samples of VK-24; *3*) standard VK-24; *4 – 6*) experimental samples of VK-23; *7*) standard VK-23; *8*, *9*) experimental samples of VK-51; *10*) standard VK-51.

and determination of the batch composition and the operating parameters for the equipment. As a result of the studies performed, the new technology was recommended and successfully implemented at the Voronezh Works of Ceramic Products [4].

The Voronezh Works produce various items of construction ceramics. Starting in 1971 a shop for producing ceramic pigments with an annual capacity of 250 tons was set up at the factory. The range of pigments produced is rather wide (Table 1). From the first day the shop was using the originally designed technology. After the approval of the technology for producing a high-temperature FZ pigment (VK-16) at the NIIStroimashkeramika Institute, it was tested at the Voronezh Works to verify the possibilities of applying it in the serial production of pigments, because the new method of batch preparation proved more economical than the one accepted in the current production.

The experiments identified a number of pigments suitable for production according to the new technology. The research clarified the process parameters and the qualitative characteristics of the pigments and the glaze coatings containing these pigments. Comparative studies of the pigments produced according to the upgraded technology with the new method of batch preparation and the traditionally produced pigments were carried out. The identical quality of the compared pigments was corroborated by the spectra of diffuse reflections of the glaze coatings, the phase compositions, the integral coefficients of diffuse reflections, and other data (Fig. 1).

The implementation of the new technology of obtaining pigments at the Voronezh Works has made it possible to virtually double the annual output without additional investments due to reduced labor and energy consumption and shortening of the technological cycle in the stage of batch preparation. The pigments can be widely used not only in construction ceramics but also in the production of house-

hold and fancy porcelain, sanitaryware (bathtubs, etc.), and plastic articles.

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